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(54) **Sulfur reduction in FCC gasoline**

Reduktion des Schwefelgehalts in Krackbenzin

Réduction de soufre dans l'essence de cracking catalytique fluidisé

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(56) References cited:  
**EP-A- 0 188 841** **EP-A- 0 385 246**  
**AU-B- 517 621** **US-A- 4 642 177**

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## Description

The present invention relates to catalytic cracking, and more specifically to catalytic cracking compositions and processes that may be used to catalytically convert high molecular weight feedstocks into valuable lower molecular weight products having reduced sulfur content.

It is generally known that catalytic cracking catalysts which comprise zeolites such as synthetic faujasite, zeolite Beta, and ZSM-5 dispersed in an inorganic oxide matrix such as silica/alumina hydrogel, sols and clay may be used to economically convert heavy hydrocarbon feedstocks such as gas-oils and/or resid into gasoline and diesel fuel.

More recently it has been disclosed that the addition of SOx reduction "additives" such as alumina, magnesium aluminate (spinel) to cracking catalyst compositions will improve the overall performance of the catalyst, particularly when used to process feedstocks that contain significant quantities of sulfur.

Canadian patent 1,117,511 describes FCC catalysts which contain free alumina hydrate, particularly alpha-alumina hydrate (boehmite) which may be used to catalytically crack hydrocarbons that contain sulfur.

U.S. Patent 4,010,116 discloses FCC catalysts which contain pseudo-boehmite aluminas that may contain crystalline trihydrate components such as bayerite and gibbsite.

While it is recognized that additives including aluminas and spinels may be added to catalytic cracking catalysts to reduce SOx emissions during the oxidation and regeneration of FCC catalyst, the industry has not developed catalytic cracking catalyst compositions that reduce the sulfur level of cracked products such as gasoline and diesel fuel.

It is therefore an object to provide improved FCC catalysts and additives which possess the ability to reduce the sulfur content of cracked products.

It is another object of the present invention to provide improved catalytic cracking compositions, additives and processes for converting sulfur-containing hydrocarbon feedstocks to low sulfur gasoline and diesel fuel.

It is yet a further object to provide a particulate FCC catalyst additive composition that may be blended with conventional zeolite-containing catalysts to reduce the sulfur content of cracked products.

These and additional objects of the invention will become readily apparent to one skilled-in-the-art from the following detailed description, specific examples, and drawings, wherein Figures 1-18 are graphic representations of Conversion vs. Gasoline sulfur content data, which illustrates the sulfur reduction capability of catalysts/additives of our invention.

Broadly, our invention contemplates zeolite catalytic cracking catalyst compositions and additives that contain a Lewis acid supported upon alumina and the use thereof to process hydrocarbon feedstocks.

More specifically, we have discovered that cracking catalyst compositions which contain from 1 to 50 weight percent of a Lewis acid such as a compound of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Tl, Pb, Bi, B, Al (other than  $Al_2O_3$ ) & Ga supported on alumina may be used to obtain gasoline fractions that have low sulfur content.

In particular, we have found that if a composition which comprises from 1 to 50 weight percent of a Lewis acid supported on alumina is added to conventional particulate zeolite containing fluid catalytic cracking (FCC) catalysts as either an integral catalyst matrix component or as a separate particulate additive having the same particle size as the conventional FCC catalyst, the catalysts may be used in the catalytic cracking of high molecular weight sulfur containing hydrocarbons feedstocks such as gas-oil, residual oil fractions and mixtures thereof to produce products such as gasoline and diesel fuel that have significantly reduced sulfur content.

Furthermore, the surface area of the Lewis acid on alumina should be as high as possible to facilitate the interaction of the sulfur species in the hydrocarbon feedstock. In other words, the dispersion of the Lewis acid on the support should be as high as possible. Therefore, compounds which can stabilize the alumina support surface area can be incorporated in the support, such as lanthana, or baria. Silica, which is also known to stabilize the surface area of alumina is detrimental to this invention.

While the mechanism by which the Lewis acid-containing alumina removes the sulfur components normally present in cracked hydrocarbon products is not precisely understood, it is believed that the Lewis Base (basic) sulfur species produced in the cracking of sulfur-containing hydrocarbons, such as gas-oil, interact with the Lewis acid on alumina by absorption or chemical reaction.

In other words, during the catalytic cracking of a sulfur-containing gas-oil at 500 to 550°C sulfur species are produced in the gasoline boiling range from the cracking reaction. These species are thiophene,  $C_1$  to  $C_4$  alkylthiophenes, tetrahydrothiophene, and propyl to hexyl mercaptans, which all have boiling points in the gasoline range. These species are Lewis bases and can interact with the Lewis acid-containing alumina. One such interaction would be adsorption of the sulfur Lewis base species to the Lewis acid-containing alumina in the riser/reactor side of the FCCU. The adsorbed species on the Lewis acid-containing alumina could then be oxidized free of the sulfur Lewis base species in the regenerator side of the FCCU, enabling more sulfur species to be adsorbed in the riser/reactor side. Another interaction would be the adsorption of the sulfur Lewis base on the Lewis acid-containing alumina, followed by cracking reactions in the riser/reactor side of the FCCU. The most likely products from these reactions would be hydrogen sulfide and hydrocarbons free of sulfur.

As shown in the examples, this invention selectively removes those sulfur species from the gasoline, such as thiophene, methylthiophenes, ethylthiophenes, propylthiophenes, and tetrahydrothiophene.

The Lewis acid-containing alumina component is prepared by reacting/impregnating an alumina substrate, which in itself has Lewis acid properties, having a surface area of 30 to 400 m<sup>2</sup>/g, with a "second" Lewis acid component selected from the group consisting of elements/compounds selected from the group consisting of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Tl, Pb, Bi, B, Al (not Al<sub>2</sub>O<sub>3</sub>), Ga and mixtures thereof.

The "desulfurizing" compositions of our invention contain from 1 to 50 weight percent and preferably 10 to 40 weight percent of the second Lewis acid component, expressed as the oxide, and the balance alumina (Al<sub>2</sub>O<sub>3</sub>).

Our Lewis acid desulfurization compositions are prepared by incorporating an alumina support having a particle size of 1 to 150 μm with a salt solution of the second Lewis acid component. Typically, aqueous solutions which contain from 10 to 20 weight percent of the Lewis acid metal salt compound, preferably the nitrates, chlorides and sulfates are used to impregnate the alumina to incipient wetness, i.e. fill the water pore volume.

The impregnated alumina is then dried at 100 to 150°C and heated (calcined) at 200 to 850°C to remove the anionic component, such as chloride, nitrate, or sulfate, thereby yielding a particulate desulfurization composition which may be added to commercial zeolite-containing "cracking" catalyst either as a component of the catalyst particulate, or as a separate particulate additive.

The hydrothermal stability of alumina substrate can be improved by stabilizing alumina with 5 to 30 weight percent La<sub>2</sub>O<sub>3</sub>. This can be achieved either by incipient-wetness impregnation of alumina particles with an aqueous solution of lanthanum or lanthanum-rich rare earth salt solution, followed by drying and calcination, or by coprecipitating well-mixed hydrous oxides of both lanthanum and aluminum, followed by washing, drying, and calcination.

Dispersion of the key Lewis acid component can be improved by including a precursor of this ingredient in the coprecipitation of well-mixed hydrous oxides of aluminum and lanthanum. For example, a key Lewis acid such as ZnO can be well-dispersed on lanthana-stabilized alumina by a co-precipitation reaction as follows: two feedstreams are simultaneously fed into a mix-pump, one acidic stream containing a mixed aqueous solution of Zn, La (or La/Nd or La-rich rare earth) salts along with an acid as needed, the other a basic solution containing a sodium aluminate solution and sodium hydroxide as needed, maintaining 8 to 9.5 pH at the mix-pump outlet. After dewatering, milling, and homogenization, the resulting slurry is spray dried, washed, dried, and calcined at 500° to 700°C to obtain attrition resistant particles compatible with FCC catalysts.

Catalysts which may be improved by the addition of our Lewis acid compositions typically comprise crystalline alumino-silicate zeolites such as synthetic faujasite i.e. type Y zeolite, type X zeolite, Zeolite Beta, ZSM-5, as well as heat treated (calcined) and/or rare-earth exchanged derivatives thereof dispersed in an inorganic oxide matrix. Zeolites which are particularly suited include calcined rare-earth exchanged type Y zeolite (CREY), the preparation of which is disclosed in US patent 3,402,996, ultrastable type Y zeolite (USY) as disclosed in US patent 3,293,192, as well as various partially exchanged type Y zeolites as disclosed in US patents 3,607,043 and 3,676,368. The catalysts may also contain molecular sieves such as SAPO and ALPO as disclosed in US patent 4,764,269. Typical catalyst compositions will include from 5 to 50 weight percent molecular sieve, 1 to 50 weight percent Lewis acid alumina dispersed in the catalyst particles, and the balance will comprise an inorganic oxide matrix which comprises binders and additives such as silica, silica alumina and alumina gels and sols as well as clay such as kaolin. Procedures that may be used to prepare FCC catalysts of the invention are disclosed in US 3,957,689, 4,126,579, 4,226,743, 4,458,023 and Canadian patent 967,136.

The desulfurizing Lewis acid additive/catalyst compositions of the present invention possess the following characteristics: A surface area of 30 to 400 m<sup>2</sup>/g as determined by BET; a bulk density of 0.4 to 0.9 g/cc; an attrition resistance of 1 to 20 DI (Davison Index) as described as follows: A 7 g sample of catalyst is screened to remove particles in the 0 to 20 micron size range. The particles above 20 microns are then subjected to a 5 hour test in the standard Roller Particle Size Analyzer using a 0.07 inch jet and 1 inch I.D. U-Tube as supplied by American Instrument Company, Silver Spring, Md. An air flow of 21 liters per minute is used. The Davison Index is calculated as follows:

$$\text{Davison Index} = \frac{\text{Wt. 0-20 micron material formed during test}}{\text{Wt. original 20 + micron fraction}} \times 100$$

The hydrocarbon feedstocks that are used typically contain from 0.1 to 2.5 weight percent, and as much as 4 weight percent sulfur. These feedstocks include gas-oils which have a boiling range of from 340 to 565°C as well as residual feedstocks and mixtures thereof.

The catalytic cracking process is conducted in conventional FCC units wherein reaction temperatures that range of from 400 to 700°C and regeneration temperatures from 500 to 850°C are utilized. The catalyst, i.e. inventory, is circulated through the unit in a continuous reaction/regeneration process during which the sulfur content of cracked gasoline and diesel fuel fraction is reduced by 5 to 100 percent.

Having described the basic aspects of the invention, the following examples are given to illustrate specific embod-

iments in which Table I shows the conditions of the microactivity testing of the samples of the invention, and Table II shows the feedstock properties of the feedstock used in the testing; and Table III shows the conditions of the circulating riser/regenerator pilot unit. All of the cracked products were analyzed for sulfur using capillary gas chromatography with an atomic emission detector, as described in Albro et al (accepted for publication in Journal of High Resolution Chromatography).

#### Example 1

An alumina substrate having a surface area of 350 m<sup>2</sup>/g, a water pore volume of 1 cc/g (SRA alumina as supplied by Grace-Davison) was impregnated with Ni to a level 10% by weight Ni as follows: 48.3 g of Ni(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O was dissolved into 100 ml H<sub>2</sub>O. 100 g of dry SRA powder was impregnated with the above Ni(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O solution. The impregnated powder was dried overnight at 110°C, then heat treated at 815°C for 4 hours. The material was then screened to obtain a fraction having a particle size range of 20 to 100 microns. The sized material was then steamed for 4 hours at 815°C with 100% H<sub>2</sub>O vapor to obtain a sample having a surface area of 106 m<sup>2</sup>/g, and an X-ray diffraction pattern which identified the presence of Ni(AlO<sub>2</sub>)<sub>2</sub>.

#### Example 2

A sample which comprised 10 weight percent Cu on alumina was prepared using the general procedure of Example 1, except that the Ni(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O in the impregnating solution was replaced with 38.6 g of Cu (NO<sub>3</sub>)<sub>2</sub>•2.5 H<sub>2</sub>O. The surface area of the material was 70 m<sup>2</sup>/g and the X-ray diffraction pattern identified the presence of Cu(AlO<sub>2</sub>)<sub>2</sub>.

#### Example 3

FCC catalyst samples were prepared by blending 3 weight percent of the samples of Examples 1 and 2 with XP-750, a commercial cracking catalyst obtained from Grace-Davison. The mixture was tested by MAT (ASTM procedure D-3907), as well as 100% XP-750 and the gasoline analyzed for sulfur. Figure 1 shows the sulfur content of the full range gasoline, T90 + 380°F, endpoint = 430°F, versus conversion. Figure 2 shows the sulfur content of cut gasoline, T90 = 300°F, endpoint = 340°F versus conversion. As shown in both figures, the sulfur content of the blends with the examples is significantly reduced.

#### Example 4

A sample which contained 10 weight percent Zn was prepared by the procedure of Example 1 except that the Ni (NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O in the impregnating solution was replaced with 49.4 g of Zn(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O. The surface area of the material was 142 m<sup>2</sup>/g and the X-ray pattern identified Zn(AlO<sub>2</sub>)<sub>2</sub>.

A blend of 3% by weight with steamed XP-750 was MAT tested as in Example 3. Figure 3 shows the sulfur content of the full range gasoline, and Figure 4 shows the cut gasoline, versus conversion. As seen in these figures, the use of Example 3 significantly reduces the sulfur content of the gasolines.

#### Example 5

This example shows that the alumina support must be free of SiO<sub>2</sub>. The incipient wetness of Grace-Davison SRS alumina, which contains 6% SiO<sub>2</sub> was determined to be 0.9 ml H<sub>2</sub>O/g SRS. 45.49 g of Zn(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O was dissolved into 237 ml H<sub>2</sub>O. 263.04 g of SRS alumina (TV = 31.57%) was impregnated with the above solution. The sample was dried overnight at 110°C, then calcined for 2 hours at 800°C. The surface area of the material was 176 m<sup>2</sup>/g. A blend containing 5 weight percent of the calcined sample and 95 weight percent steamed (1500°F, 100% H<sub>2</sub>O, 4 hours) XP-750 was prepared and tested by MAT, using 100% XP-750 as the base case. Figure 5 shows the sulfur content of the full range gasoline, and Figure 6 shows the sulfur content of the cut gasoline at T90 = 300°F, versus conversion. As shown when silica is present in the alumina support, the performance of the invention is degraded.

#### Example 6

A catalyst composition consisting of zinc oxide/lanthana-neodymia/alumina was prepared by coprecipitation as follows: an acidic solution containing 68.88 g of ZnO and 34.44 g of (La/Nd)<sub>2</sub>O<sub>3</sub> was prepared from their nitrates along with 9.6 g of straight nitric acid, and was diluted with DI-water to 98.4 ml. A dilute sodium aluminate solution containing 68.88 g Al<sub>2</sub>O<sub>3</sub> was also readied by diluting 340.99 g of plant-made solution with DI-water to 984 ml. These two solutions were fed into a beaker with 400 g of DI-water at 38-43°C, at an equal rate of 40 ml/min., with good agitation. Feeding

another feedstream of 16% sodium hydroxide solution directly into the blender, pH of the resulting slurry of mixed hydrous oxide was maintained at 8.5-8.7 while maintaining the slurry at 38 -43°C through the runoff. After 15 min. aging under this condition, pH of the slurry was raised to 9.0 with dilute sodium hydroxide, and the slurry was dewatered immediately using a Buchner funnel. The filtercake was then washed three times with 1.7 liters of 80°C DI-water. The resulting filtercake was dried overnight in 115°C oven, crushed, and sifted. Particles of 80 - 200 meshes were air calcined for 2 hours at 704°C. The resulting material was 74 m<sup>2</sup>/g BET (N<sub>2</sub>) surface area, and had the following composition (weight %): 40.72% ZnO, 0.05% Na<sub>2</sub>O, 16.24% La<sub>2</sub>O<sub>3</sub>, 1.89% Nd<sub>2</sub>O<sub>3</sub>, 18.18% total RE<sub>2</sub>O<sub>3</sub>, 0.15% SO<sub>4</sub>, and 40.81% Al<sub>2</sub>O<sub>3</sub>. Powder X-ray diffraction scan largely exhibited a pattern characteristic of ZnO and the presence of La<sub>2</sub>O<sub>3</sub>. This example was then blended with steamed XP-750 and MAT tested as in the previous examples. Figures 7 and 8 show the full range and cut gasoline sulfur levels for the blend with Example 6 and neat XP-750. As seen, a reduction in the sulfur content of the gasolines is achieved.

#### Example 7

This example shows the utility of this invention in circulating FCC riser/regenerator pilot unit testing. 15 kg of Davison SRA alumina was slurried in H<sub>2</sub>O to nominally 20% solids. The slurry was peptized with 35% HCl using 0.15 mols HCl/mole of Al<sub>2</sub>O<sub>3</sub> in the slurry. The slurry was then sand milled, and peptized again with 0.1 moles HCl/mole of Al<sub>2</sub>O<sub>3</sub>. The slurry was then spray dried. 2 kg of the spray dried alumina was calcined for 2 hours at 538°C to remove moisture and HCl. 100 g of the above material was impregnated with 45.49 g of Zn(NO<sub>3</sub>)<sub>2</sub>•6 H<sub>2</sub>O dissolved in 100 g H<sub>2</sub>O. This impregnation was repeated 13 times, then combined, making Example 7. The combined materials were calcined for 3 hrs at 704°C to pre-treat the materials for testing.

A charge of 2300 g of XP-750 was loaded into the Davison Circulating Riser (DCR) and a yield curve at various conversions was run. 255.5 g of pretreated Example 7 was then added to the inventory of the DCR to give a nominal blend of 10% of Example 7 with 90% of XP-750. Another yield curve was run by varying the conversion. The gasolines from the riser testing were analyzed for sulfur in a similar fashion to the previous MAT studies. Figures 9 and 10 show the full range and cut gasolines for neat XP-750 and the 10% blend with Example 7. Again, a clear reduction in the sulfur content of the gasolines is observed with this invention in riser/regenerator pilot unit testing. To further illustrate the effectiveness of this invention Figures 11 - 18 show the concentrations of the individual classes of sulfur species in the gasoline fraction from the pilot unit testing. These classes are, respectively, the C<sub>3</sub> to C<sub>6</sub> mercaptans, thiophene, methylthiophenes, tetrahydrothiophene, C<sub>2</sub> alkyl thiophenes, C<sub>3</sub> alkyl thiophenes, C<sub>4</sub> alkyl thiophenes, and benzothiophene. In all cases, a reduction of the concentrations of the compounds is observed. Furthermore, an increase in gasoline yield, which would account for the reduction in concentration in a simple way was not observed.

TABLE I

Conditions for Microactivity Testing (MAT)			
Temperature, °F		980	
nominal catalyst charge, gr.		5	
cat to oil weight ratios	2	3	4
WHSV, hr <sup>-1</sup>	60	40	30

TABLE II

Feed Properties	
°API	27.8
Aniline Point, °F	187
Sulfur, wt. %	0.474
Total Nitrogen, wt. %	0.07
Basic Nitrogen, wt. %	0.02
Conradson Carbon, wt. %	0.16
Ni, ppm	0.14
V, ppm	0.1

TABLE II (continued)

Feed Properties	
FE, ppm	0.4
Cu, ppm	<0.1
Simulated Distillation, vol.% °F	
IBP	338
5	444
10	486
20	549
30	603
40	640
50	694
60	734
70	786
80	840
90	910
95	961
FBP	1065
K factor	11.68

TABLE III

Testing Conditions of the Davison Circulating Riser (DCR) FCC Pilot Plant	
Adiabatic Operating Mode	
Riser Outlet Temperature -	970°F
Feed Preheat Temperature -	250 - 750°F
Regenerator Temperature -	1300°F
Reactor Pressure -	25 psig

Catalyst Deactivation of the XP-750:

4 hrs./1500°F/100% 0 psig Steam

Fluid Bed Steaming

### Claims

1. A catalytic cracking catalyst composition which comprises (a) a molecular sieve dispersed in an inorganic oxide matrix, and (b) a Lewis acid-containing alumina component consisting essentially of 1 to 50 wt.%, expressed as oxide based on the total weight of Lewis acid and alumina in said component, of a Lewis acid selected from the group comprising elements and compounds of Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Tl, Pb, Bi, B, Al (other than  $Al_2O_3$ ) and Ga, said Lewis acid being supported on alumina.
2. The composition of claim 1, wherein said component is included as a separate particulate additive.
3. The composition of claim 1, wherein said component is included in said matrix.
4. The composition of claim 1 which contains about 1 to 50 wt.% of said component.
5. The composition of claim 1, wherein said molecular sieve is synthetic faujasite and said catalyst composition contains from 1 to 50 wt.% of said component, from 5 to 50 wt.% synthetic faujasite, from 10 to 60 wt.% clay, and from 10 to 30 wt.% of an inorganic oxide binder selected from the group consisting of silica, alumina and silica-

alumina, hydrogels and sols.

6. The composition of claim 1, wherein the alumina has a surface area of 30 to 400 m<sup>2</sup>/g.
- 5 7. The composition of claim 1, wherein the alumina is lanthana-stabilized.
8. The composition of claim 1, wherein said Lewis acid is Zn.
9. The composition of claim 7, wherein the composition has a particle size of 20 to 140 µm, a DI of 1 to 20, and a  
10 bulk density of 0.4 to 0.9.
10. A method for the catalytic cracking of sulfur-containing hydrocarbons which comprises reacting a hydrocarbon feedstock with the catalyst of claims 1 to 9 and removing gasoline fractions having a reduced sulfur content.
- 15 11. The method of claim 10, wherein said feedstock contains up to 4 wt.% S.
12. Use of a composition comprising the alumina-supported Lewis acid component of claim 1 in fluid catalytic cracking processes to lower the level of sulfur in gasoline resulting from said processes.
- 20 13. The use of claim 10, wherein said alumina is lanthana-stabilized.
14. Use of a composition according to claims 1 to 9 for producing low sulfur gasoline and diesel fuel by catalytic cracking of hydrocarbons.
- 25 15. Use according to claim 14, characterized in that the hydrocarbon contains 0.1 to 5 wt.% sulfur and that the sulfur content of the cracked gasoline or diesel fuel is reduced by 5 to 100%.

#### Patentansprüche

- 30 1. Katalytische Crack-Katalysator-Zusammensetzung, enthaltend (a) ein in einer anorganischen Oxid-Matrix dispergiertes Molekularsieb und (b) eine eine Lewis-Säure enthaltende Aluminiumoxidkomponente, die im wesentlichen aus 1 bis 50 Gew.-%, ausgedrückt als Oxid basierend auf dem Gesamtgewicht an Lewis-Säure und Aluminiumoxid in der Komponente, einer Lewis-Säure besteht, die aus der Gruppe ausgewählt ist, welche Elemente und Verbindungen von Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Tl, Pb, Bi, B, Al (anders als Al<sub>2</sub>O<sub>3</sub>) und Ga enthält, wobei die Lewis-Säure auf Aluminiumoxid als Träger aufgebracht ist.
- 35 2. Zusammensetzung nach Anspruch 1, in der die Komponente als separates partikuläres Additiv beigelegt ist.
- 40 3. Zusammensetzung nach Anspruch 1, in der die Komponente in der Matrix enthalten ist.
4. Zusammensetzung nach Anspruch 1, enthaltend etwa 1 bis 50 Gew.-% der Komponente.
- 45 5. Zusammensetzung nach Anspruch 1, in der das Molekularsieb ein synthetisches Faujasit ist und die Katalysator-Zusammensetzung 1 bis 50 Gew.-% der Komponente, 5 bis 50 Gew.-% synthetisches Faujasit, 10 bis 60 Gew.-% Ton und 10 bis 30 Gew.-% eines anorganischen Oxid-Bindemittels enthält, das aus der Gruppe ausgewählt ist, die aus Siliciumdioxid, Aluminiumoxid und Siliciumdioxid-Aluminiumoxid, Hydrogelen und Solen besteht.
- 50 6. Zusammensetzung nach Anspruch 1, in der das Aluminiumoxid eine Oberfläche von 30 bis 400 m<sup>2</sup>/g aufweist.
7. Zusammensetzung nach Anspruch 1, in der das Aluminiumoxid durch Lanthanoxid stabilisiert ist.
8. Zusammensetzung nach Anspruch 1, in der die Lewis-Säure Zn ist.
- 55 9. Zusammensetzung nach Anspruch 7, in der die Zusammensetzung eine Partikelgröße von 20 bis 140 µm, einen DI von 1 bis 20 und eine Schüttdichte von 0,4 bis 0,9 hat.
10. Verfahren für das katalytische Cracken von schwefelhaltigen Kohlenwasserstoffen, welches das Reagieren eines

Kohlenwasserstoff-Einsatzmaterialien mit einem Katalysator gemäß den Ansprüchen 1 bis 9 und das Abtrennen der Benzinfraktionen mit einem verminderten Schwefelgehalt umfaßt.

11. Verfahren gemäß Anspruch 10, bei dem das Einsatzmaterial bis zu 4 Gew.-% S enthält.
12. Verwendung einer Zusammensetzung enthaltend die auf Aluminiumoxid als Träger aufgebrachte Lewis-Säure-Komponente von Anspruch 1 in katalytischen Fließbett-Krackverfahren zur Verringerung des Schwefelgehalts in dem aus dem Verfahren resultierenden Benzin.
13. Verwendung nach Anspruch 10, bei der das Aluminiumoxid durch Lanthanoxid stabilisiert ist.
14. Verwendung einer Zusammensetzung gemäß den Ansprüchen 1 bis 9 zur Herstellung von Benzin und Dieselmotortreibstoff mit geringem Schwefelgehalt durch katalytisches Cracken von Kohlenwasserstoffen.
15. Verwendung nach Anspruch 14, dadurch gekennzeichnet, daß der Kohlenwasserstoff 0,1 bis 5 Gew.-% Schwefel enthält und daß der Schwefelgehalt des gekrackten Benzins oder Dieselmotortreibstoffs um 5 bis 100 % vermindert ist.

# Revendications

1. Composition d'un catalyseur de craquage catalytique qui comprend (a) un tamis moléculaire dispersé dans une matrice d'oxyde inorganique, et (b) un composant d'alumine contenant un acide de Lewis consistant essentiellement en 1 à 50% en poids, exprimé comme oxyde en se basant sur le poids total de l'acide de Lewis et de l'alumine dans ledit composant, d'un acide de Lewis sélectionné dans le groupe comprenant les éléments et les composés de Ni, Cu, Zn, Ag, Cd, In, Sn, Hg, Tl, Pb, Bi, B, Al (autre que  $Al_2O_3$ ) et Ga, ledit acide de Lewis étant supporté sur de l'alumine.
2. Composition de la revendication 1, où ledit composant est incorporé en tant qu'additif particulaire séparé.
3. Composition de la revendication 1, où ledit composant est incorporé dans ladite matrice.
4. Composition de la revendication 1 qui contient environ 1 à 50% en poids dudit composant.
5. Composition de la revendication 1, où ledit tamis moléculaire est de la faujasite synthétique et ladite composition du catalyseur contient de 1 à 50% en poids dudit composant, de 5 à 50% en poids de faujasite synthétique, de 10 à 60% en poids d'argile et de 10 à 30% en poids d'un liant d'oxyde inorganique sélectionné dans le groupe consistant en silice, alumine et aluminosilicate, hydrogels et sols.
6. Composition de la revendication 1, où l'alumine a une aire superficielle de 30 à 400  $m^2/g$ .
7. Composition de la revendication 1, où l'alumine est stabilisée à l'oxyde de lanthane.
8. Composition de la revendication 1, où ledit acide de Lewis est Zn.
9. Composition de la revendication 7, où la composition a une grandeur de particules de 20 à 140  $\mu m$ , une valeur de DI de 1 à 20, et une densité apparente de 0,4 à 0,9.
10. Méthode pour le craquage catalytique d'hydrocarbures contenant du soufre qui comprend la réaction d'une charge d'alimentation d'hydrocarbures avec le catalyseur des revendications 1 à 9 et l'enlèvement des fractions d'essence ayant une teneur réduite en soufre.
11. Méthode de la revendication 10, où ladite charge d'alimentation contient jusqu'à 4% en poids de S.
12. Utilisation d'une composition comprenant le composant d'acide de Lewis supporté sur de l'alumine de la revendication 1 dans des procédés de craquage catalytique fluide pour abaisser le niveau du soufre dans l'essence résultant desdits procédés.
13. Utilisation de la revendication 10, où ladite alumine est stabilisée à l'oxyde de lanthane.



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14. Utilisation d'une composition selon les revendications 1 à 9 pour produire de l'essenc et du combustible diesel à faible teneur en soufre par craquag catalytique des hydrocarbures.

5 15. Utilisation selon la revendication 14, caractérisée en ce que l'hydrocarbur contient 0,1 à 5% en poids de soufre et en ce que la teneur en soufre de l'essence craquée ou du combustible diésel est réduit de 5 à 100%.

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FIG. 1

Conversion vs. Gasoline Sulfur  
for Full Range Gasoline, Endpoint = 430 °F

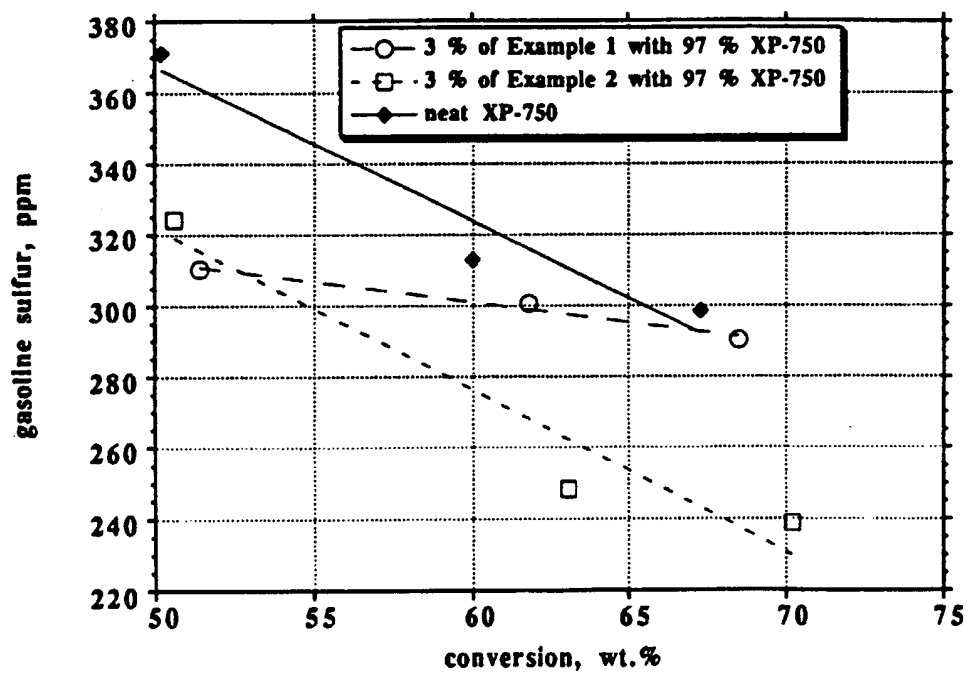
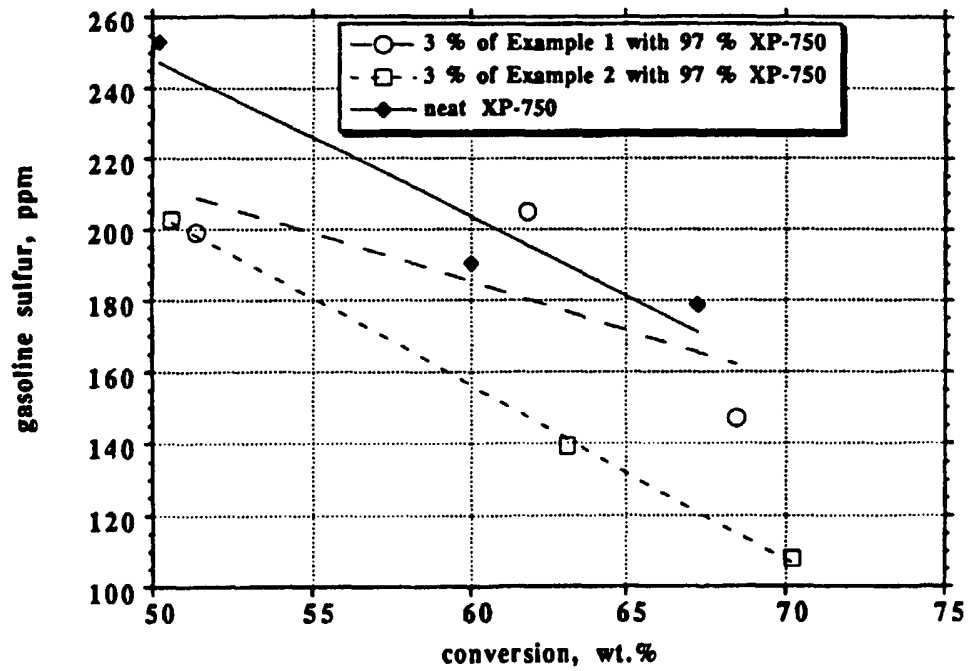


FIG. 2

Conversion vs. Gasoline Sulfur  
for T90 = 300 °F Cut Gasoline



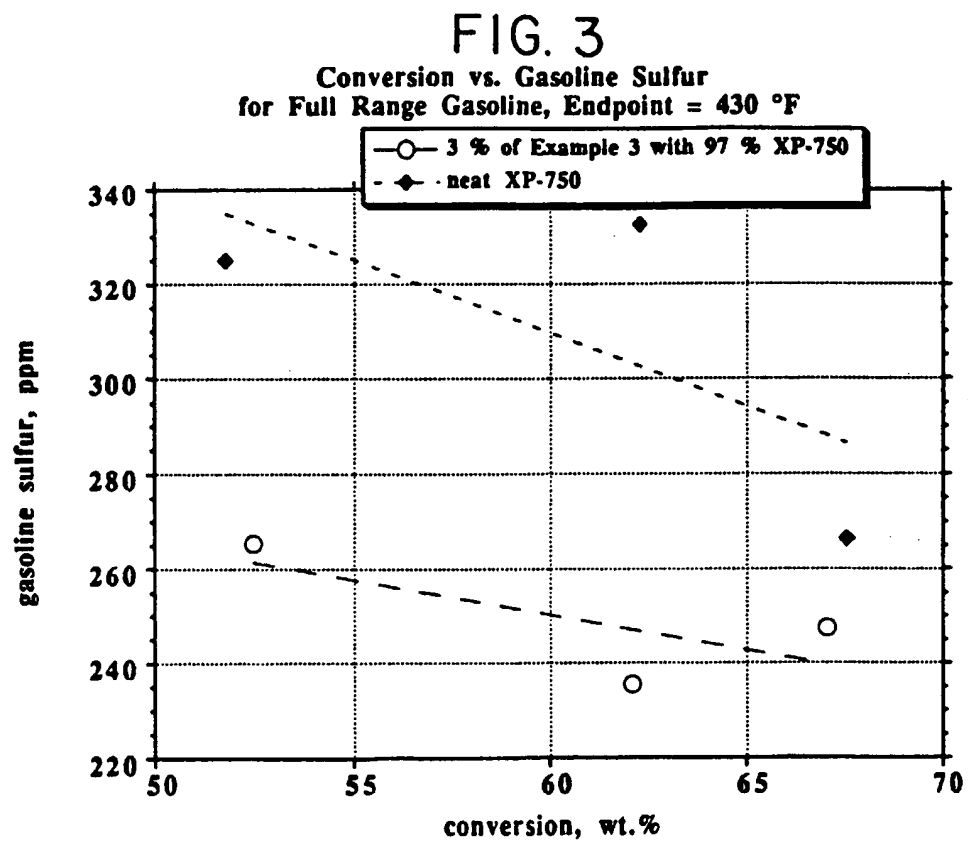


FIG. 4  
Conversion vs. Gasoline Sulfur  
for T90 = 300 °F Cut Gasoline

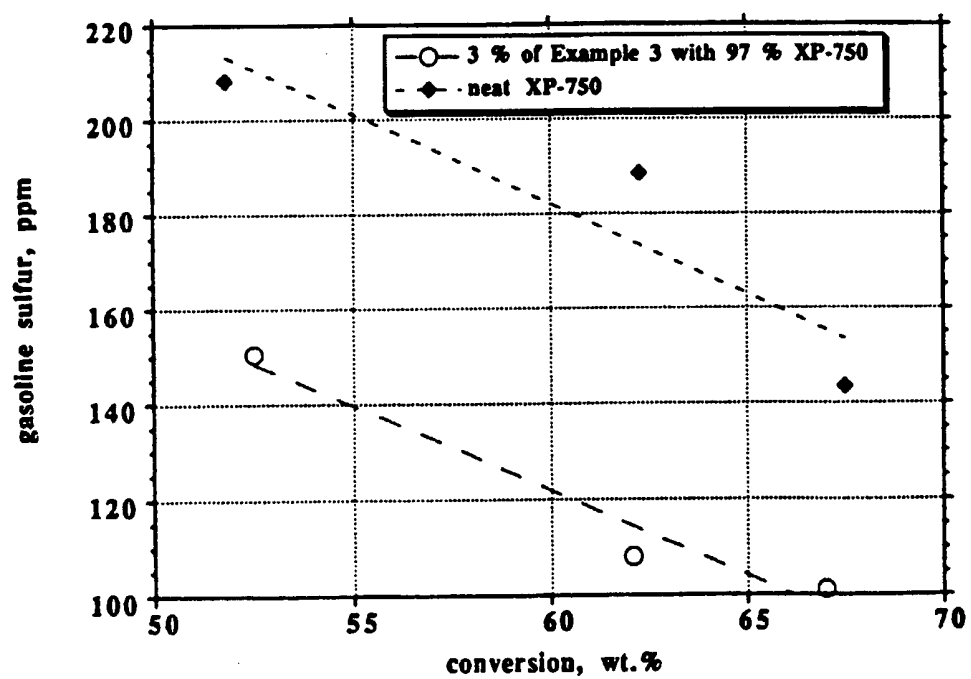


FIG. 5

Conversion vs. Gasoline Sulfur  
for Full Range Gasoline, Endpoint = 430 °F

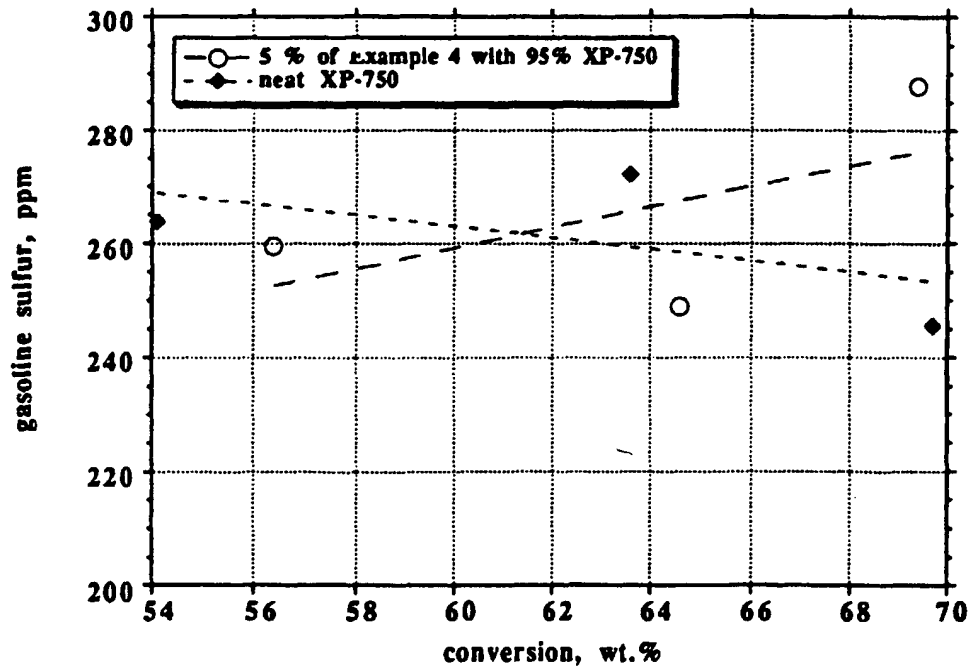


FIG. 6

Conversion vs. Gasoline Sulfur  
for T<sub>90</sub> = 300 °F Cut Gasoline

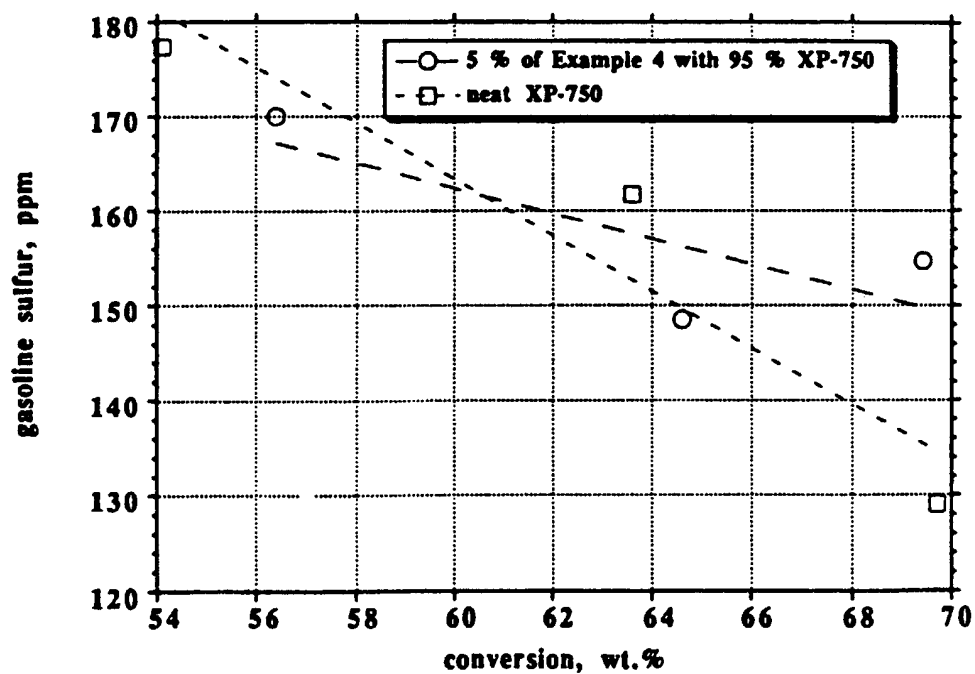


FIG. 7

Conversion vs. Gasoline Sulfur  
for Full Range Gasoline, Endpoint = 430 °F

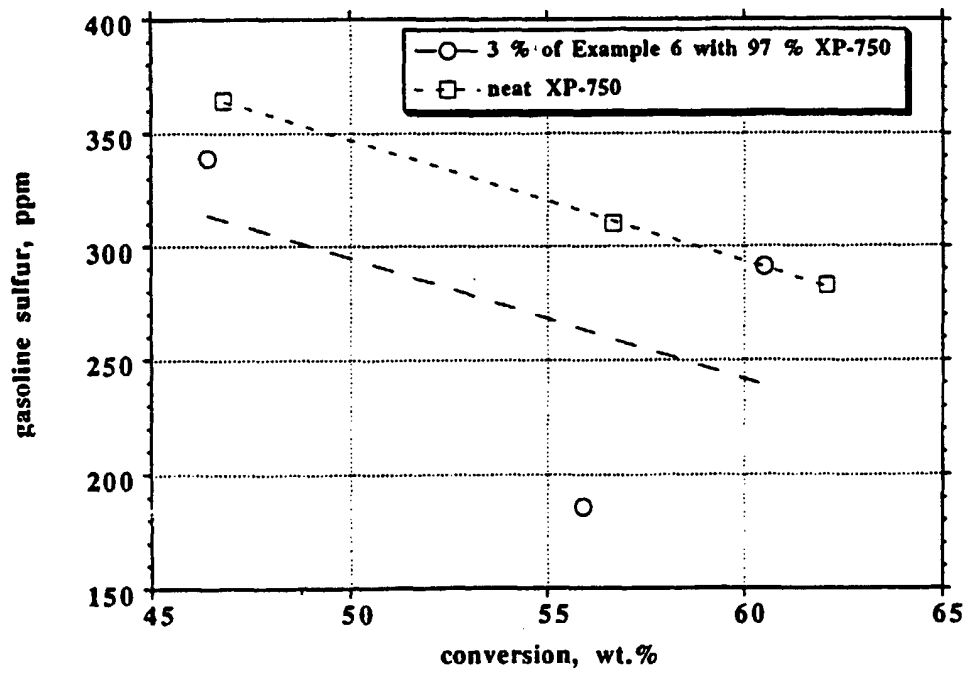
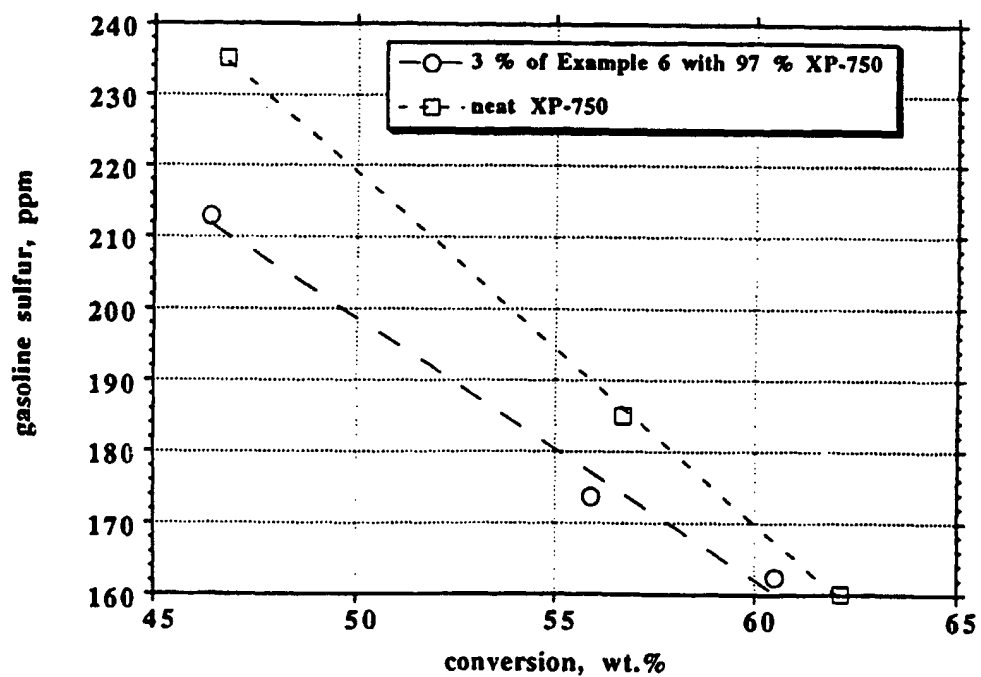




FIG. 8

Conversion vs. Gasoline Sulfur  
for T90 = 300 °F Cut Gasoline



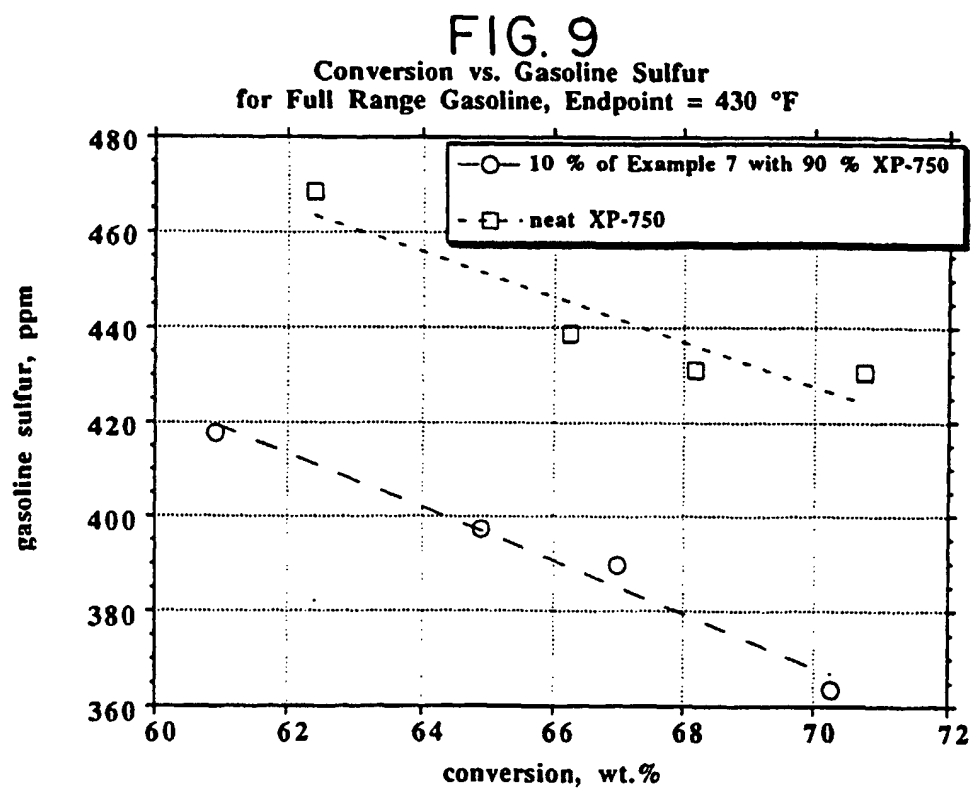
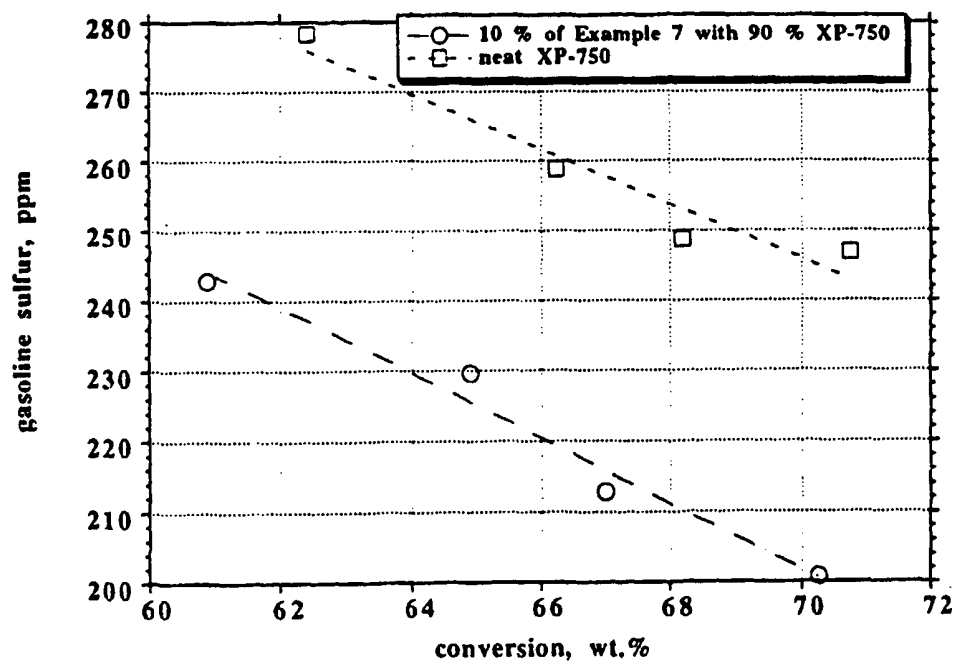


FIG. 10

Conversion vs. Gasoline Sulfur  
for T<sub>90</sub> = 300 °F Cut Gasoline



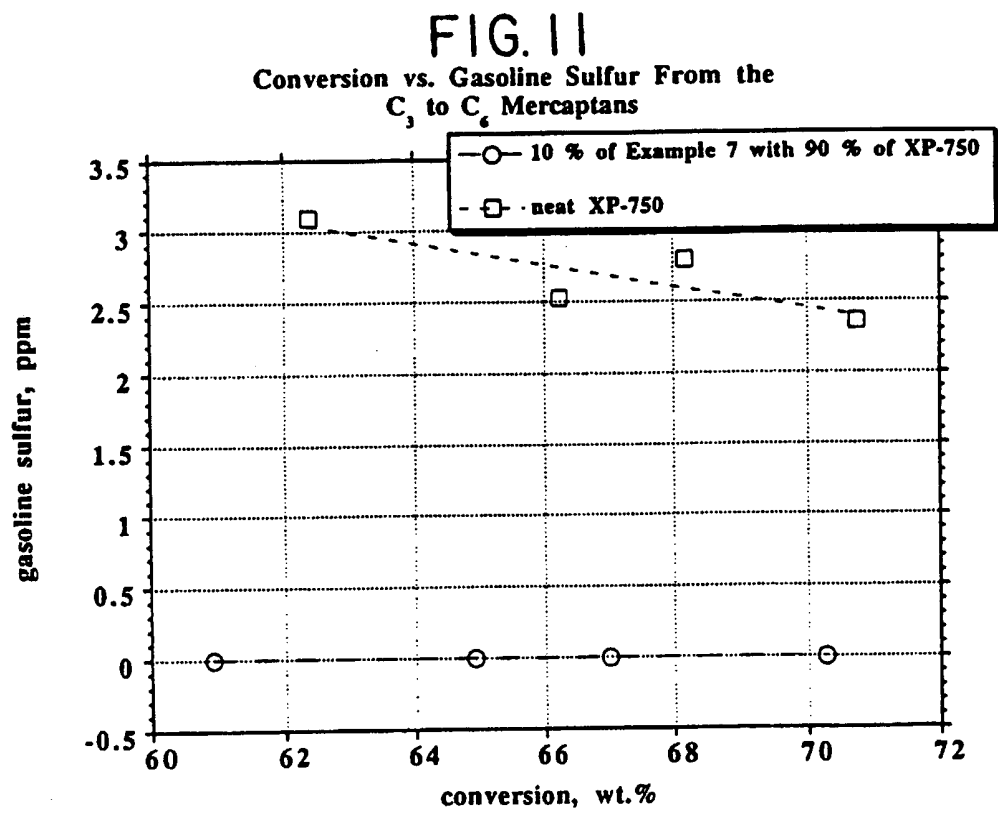
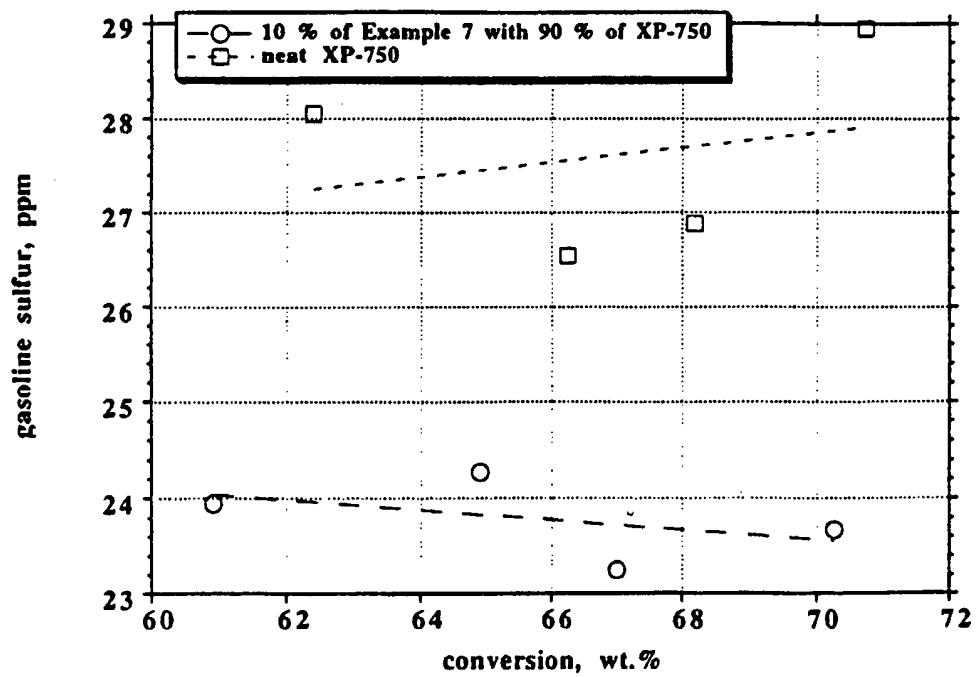


FIG. 12

Conversion vs. Gasoline Sulfur From Thiophene



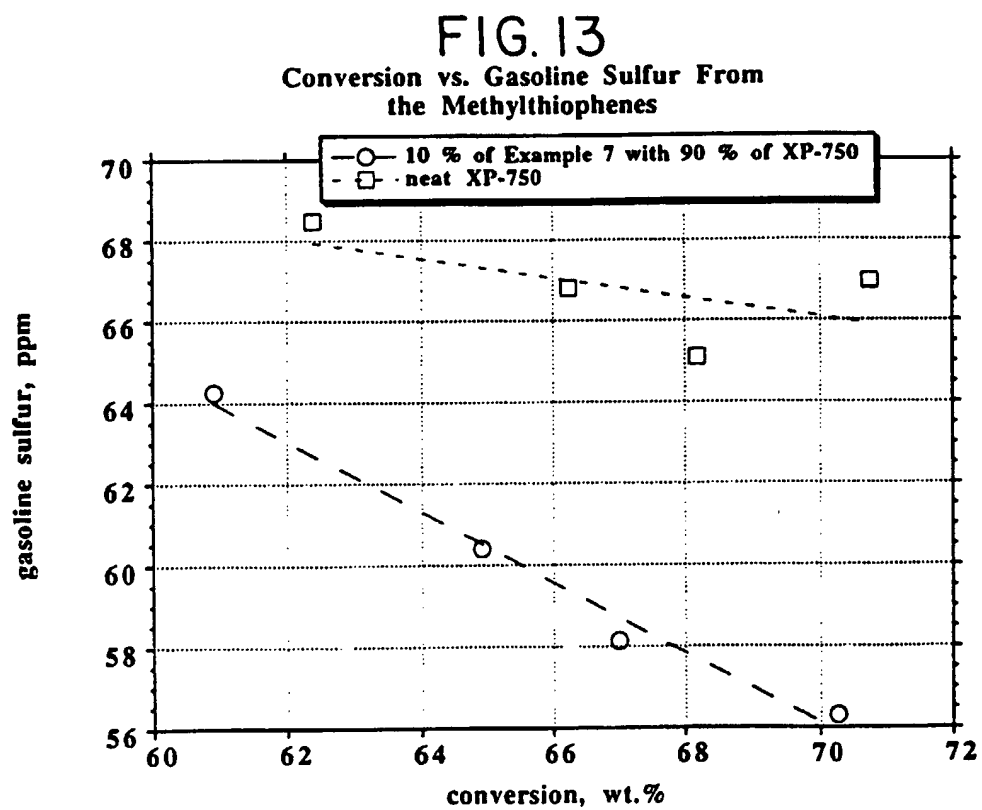


FIG. 14

Conversion vs. Gasoline Sulfur From  
Tetrahydrothiophene

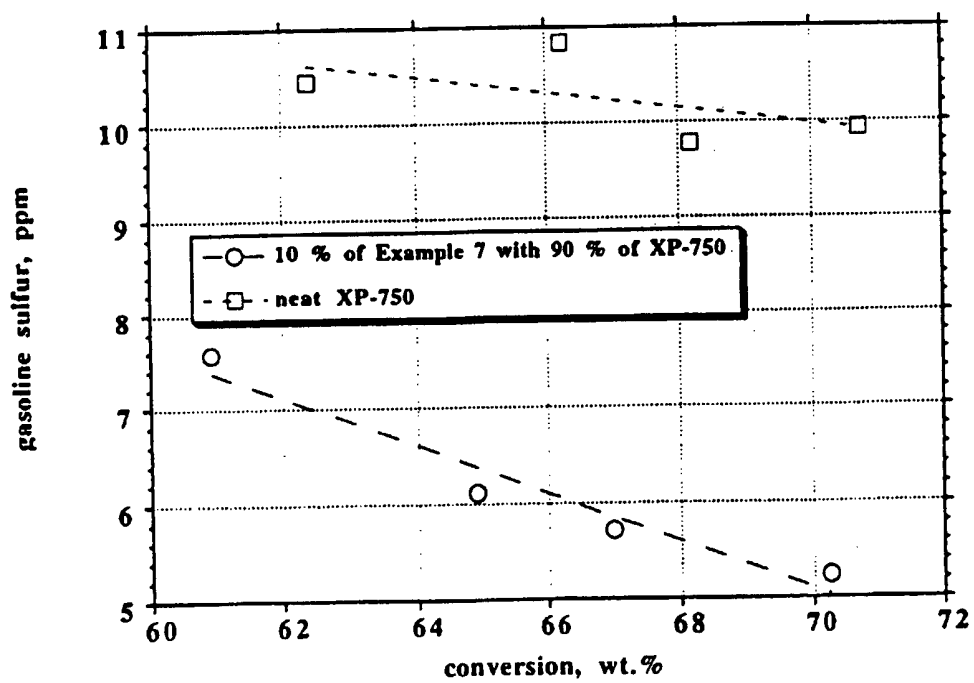


FIG. 15

Conversion vs. Gasoline Sulfur From  
the C<sub>2</sub> thiophenes

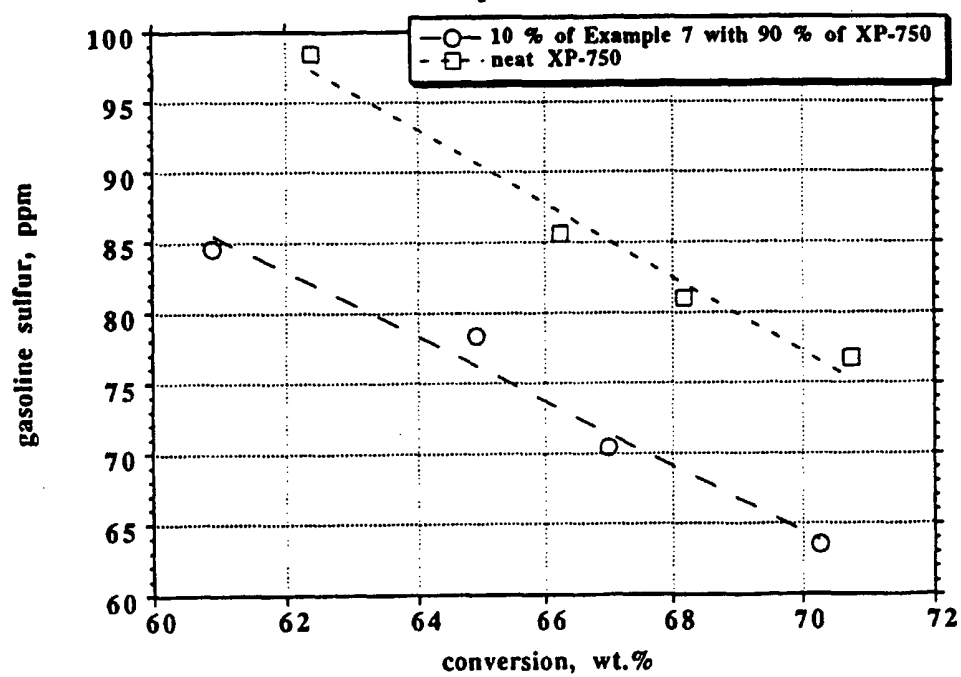
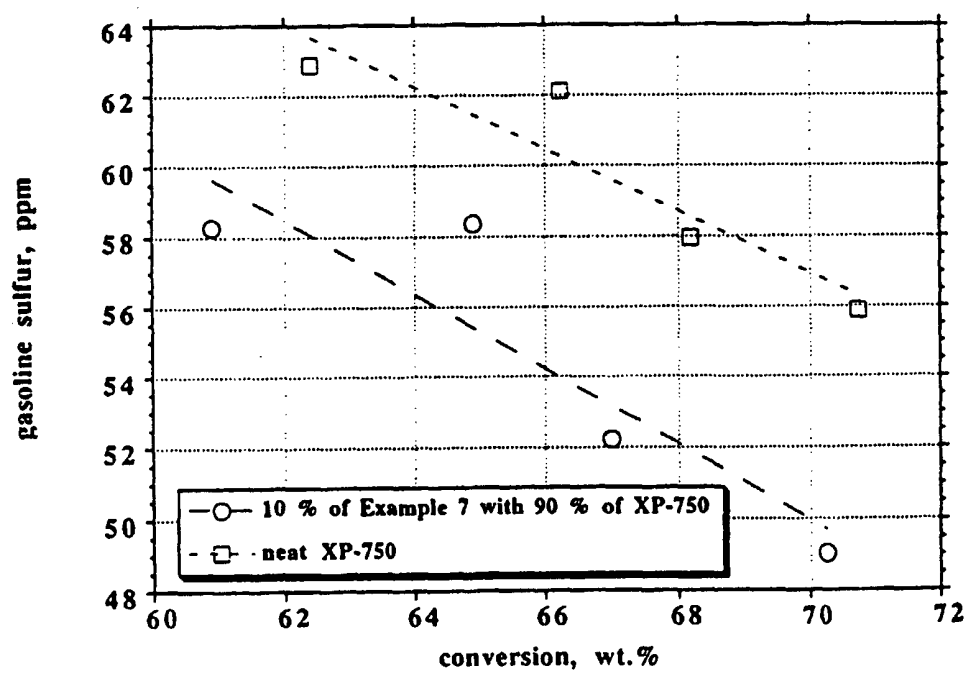


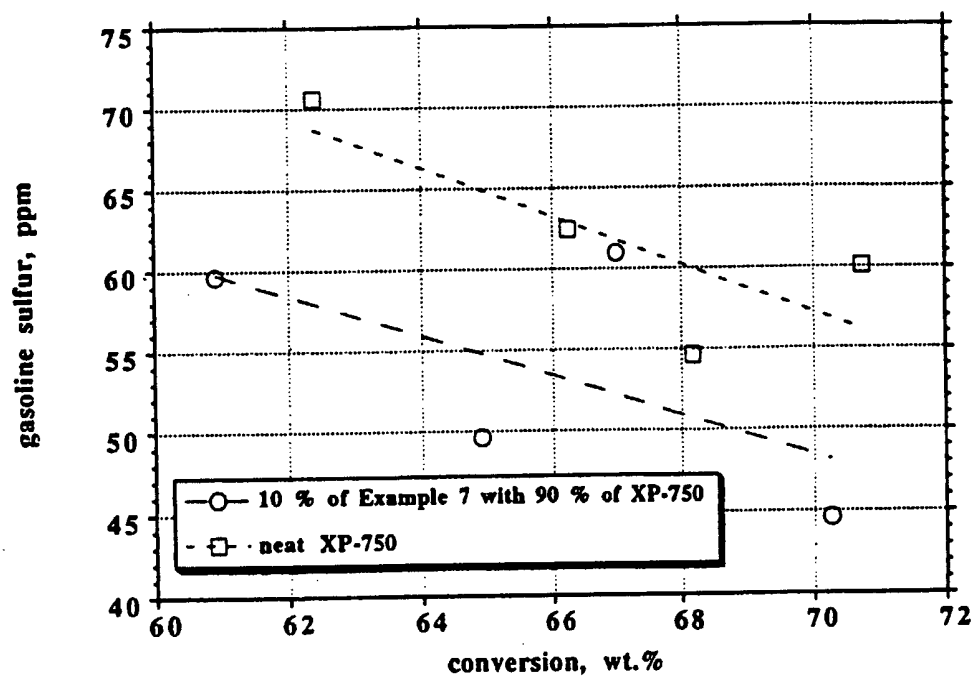


FIG. 16

Conversion vs. Gasoline Sulfur From  
the C<sub>3</sub> thiophenes



**FIG. 17**  
Conversion vs. Gasoline Sulfur From  
the C<sub>4</sub> thiophenes



**FIG. 18**  
Conversion vs. Gasoline Sulfur From  
Benzothiophene

